Extraction and X-ray analysis of phases in aluminium alloys

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The extraction of precipitates and second phase insoluble intermetallic or metalloid compounds from three commerical aluminium alloys was achieved by anodic dissolution of the aluminium alloy matrix in a methanolic electrolyte containing benzoic acid, oxine and chloroform. Investigated were Aluminium Association alloy 7075 containing principally Al–Zn–Mg–Cu, alloy 6061 containing principally Al–Si, and alloy 2011 containing principally Al–Cu. X-ray diffraction of the extracted residues using the Debye–Scherrer method, identified the compounds $MnAl_6$, MgO and Mg_2Si in the 7075 alloy in the aged condition, the insoluble phase $Mn_{12}Si_7Al_5$ in the 6061 alloy in both the solution heat-treated and aged conditions. In the 2011 alloy the primary precipitate, $CuAl_2$, was extracted in the aged condition and the lattice parameters for this tetragonal compound were determined to be $a = 6.064$ Å and $c = 4.874$ Å: Metallic bismuth also was identified in the extraction from this alloy. Several lines, believed to represent an unknown ternary or higher compound, could not be identified.

1. Introduction

The precipitation processes in aluminium alloys are well understood and the identification and analysis of those precipitates primarily responsible for the strengthening effects during precipitation heat-treatment is reasonably complete. Less well understood, however, are the roles played by the minor alloying elements involved in the formation of metalloids, dispersoids, and insolubles which are important in controlling, among other things, fineness of grain structure, and the formation of precipitate-free zones around grain boundaries. Previously, the study of most of these compounds has been necessarily performed through *in situ* methods, although anodic dissolution of aluminium alloys in strong acids [1], or simple dissolution in solutions of iodated methanol have been tried [2]. In addition, extraction-replica techniques have been used to produce small samples of extracted phases for electron microscopy [3, 4]. While a great variety of both chemical and electrochemical methods have been developed for the extraction of secondary phases from steels and nickel-base alloys [5–12], until recently, no equivalent anodic dissolution techniques using a relatively inactive electrolyte have been available for aluminium alloys. It has lately been found, however, that methanolic solutions of benzoic acid, oxine and chloroform can be used to selectively remove the aluminium alloy matrix by galvanostatic anodic dissolution, while leaving second phase particles intact [13].

This method has been applied to the examination of constituent phases in three commercial aluminium alloys; Aluminium Association alloy 7075 containing principally Al–Zn–Mg–Cu, alloy

TABLE I Chemical limit compositions of aluminium alloys (wt%)

Alloy	Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Others	Al
2011	0.40	0.7	5.0–6.0	–	–	–	0.30	–	0.15[a]	Remainder
6061	0.4–0.8	0.7	0.15–0.40	0.15	0.8–1.2	0.04–0.35	0.25	0.15	0.15	Remainder
7075	0.40	0.50	1.2–2.0	0.3	2.1–2.9	0.18–0.35	5.1–6.1	0.20[b]	0.15	Remainder

[a]Also contains 0.20–0.60 wt% each of Pb and Bi.
[b]Zr plus Ti 0.25 wt% maximum.

6061 containing principally Al–Si, and alloy 2011 containing principally Al–Cu.

2. Experimental procedure

Chemical limit compositions for the three commercial alloys examined are listed in Table I. Solution heat-treatment was carried out in an open-ended vertical furnace, which facilitiated rapid quenching into a bath of ice-water, and ageing was carried out in a KNO_3–$LiNO_3$ salt bath. The 7075 alloys were solution heat-treated for 2 h at 500° C and aged for 24 h at 300° C; solution heat-treatment of the 6061 alloys was performed at 535° C for 24 h and ageing at 300° C for 2 h. The 2011 alloys were solution heat-treated at 520° C for 3 h and aged at 315° C for 4 h. These treatments produce, in all cases, an aged condition – that is, aged beyond maximum hardness conditions – and were chosen so as to complete and bring to near equilibrium all precipitation processes likely to occur in these alloys.

The majority of the precipitate extractions were carried out in oxine solution consisting of 15 g 8-hydroxyquinoline (oxine), 60 g benzoic acid, 60 ml chloroform and 165 ml methanol. The dissolution of the aluminium alloy matrix was aided by anodically driving the reaction at a current density of approximately $10 \, mA \, cm^{-2}$; pure aluminium was used as a counter electrode [13]. A solution containing 10 g of iodine in 100 ml of methanol also was used for extraction purposes [2]; however, the latter proved considerably more active than the oxine solution and reacted with most of the constituent phases as well as the aluminium matrix.

Once extracted, the undissolved phases were washed of residual organic solution with methanol and chloroform. X-ray data were obtained with a 114 mm Debye-Scherrer camera, using copper $K\alpha$ radiation.

3. Results and discussion

The 7075 alloy in the solution heat-treated and aged condition was extracted in the oxine solution. The resulting X-ray data from the extracted phases are shown in Table II; the d-spacings and relative intensities of all the reflections observed are listed, along with hkl values and expected relative intensities for each component identified. However for all alloys, as may be seen, there are one or more X-ray lines which remain unknown. The insoluble phases $MnAl_6$ and MgO could be readily identified, as was a small quantity of Mg_2Si. The Mg_2Si may or may not be insoluble at the 500° C solution heat-treatment temperature and could be a precipitation product [14]. Some ambiguity may arise with the d-spacings of $MnAl_6$ compound since Fe may substitute for the Mn, and previous results have suggested that the compound has some solubility for zinc [1, 14]. From consideration of the quaternary phase diagram of the Al–Zn–Mg–Cu system [15], the most likely precipitation product at 300° C would be the s-phase, Al_2CuMg. It is apparent from the results obtained that the s-phase dissolves in the oxine solution, and this makes a study of the primary precipitate phase by this method impossible. However, the more stable secondary phases can be examined with considerably less difficulty than if the s-phase, which produces a large number of X-ray reflections, were present.

The 6061 alloy was extracted in the oxine solution in both the solution heat-treated and aged conditions. In both cases the product was an insoluble intermetallic compound $Mn_{12}Si_7Al_5$, Table III. Also, the absence of Mg_2Si in either the solution heat-treated or aged condition suggests that it is appreciably dissolved in the oxine solution.

The 2011 alloy was extracted in the solution heat-treated and aged condition; the primary precipitate, $CuAl_2$, and metallic bismuth were identified, Table IV. Attempts to index the remaining lines based on binary, ternary, and higher compounds of the elements Al, Cu, Zn, Bi, Pb, Fe, Si, O, H and N were unsuccessful, however. The X-ray data obtained for the $CuAl_2$ were sufficiently

TABLE II X-ray data from aluminium alloy 7075, solution heat-treated 2 h at 500° C and aged 24 h at 300° C; extracted in oxine solution.

Line	d(Å)	I/I_0	MnAl$_6$	I/I_0(MnAl$_6$)	MgO	I/I_0(MgO)	Mg$_2$Si	I/I_0(Mg$_2$Si)	(Al,Fe,Si)H	I/I_0[(Al,Fe,Si)H]
1	4.877	20								
2	4.403	10	0 0 2	10						
3	4.277	10	1 1 1	10						
4	3.747	15	0 2 0	10						
5	3.345	5								
6	3.264	20	2 0 0	10						
7	3.033	5	2 0 1	6						
8	2.845	5	0 2 2	6						
9	2.603	5	2 0 2	20						
10	2.513	15	1 1 3	20						
11	2.437	10	2 2 0	6	1 1 1	10				
12	2.347	5	1 3 0	10						
13	2.247	30					2 2 0	100		
14	2.201	5	0 0 4	20						
15	2.168	10	2 0 3	20					0 4 7	50
16	2.136	30							0 5 1, 1 4 5	40
17	2.101	100			2 0 0	100			0 5 2	50
18	2.055	60	3 1 0	100					1 4 6, 3 3 1	100
19	2.007	50	3 1 1	50					0 5 5, 2 4 3	30
20	1.892	5	0 2 4	16						
21	1.874	10	2 2 3, 0 4 0, 3 1 2	30						
22	1.813	15	1 3 3, 2 0 4	10						
23	1.720	5	0 4 2	10						
24	1.634	5	2 2 4, 3 3 0	10						
25	1.597	5					4 0 0	20		
26	1.558	5	2 0 5	6						
27	1.518	5	4 0 2, 3 1 4	2						
28	1.489	50			2 2 0	52				
29	1.460	5					3 3 1	6		
30	1.416	5	2 4 3, 4 0 5	16						
31	1.403	5								
32	1.363	5								
33	1.334	5								
34	1.303	10					4 2 2	40		
35	1.278	10			3 1 1	4				
36	1.257	5								
37	1.246	5								
38	1.229	5					5 1 1	5		
39	1.216	20			2 2 2	12				
40	1.196	5								
41	1.166	5								
42	1.153	5								
43	0.969	5			3 3 1	2				
44	0.942	5			4 2 0	17				
45	0.902	5								
46	0.879	5								
47	0.860	15			4 2 2	15				
48	0.810	15			5 1 1	3				

TABLE III X-ray data from aluminium alloy 6061, solution heat-treated for 2 h at 535° C and aged for 24 h at 300° C; extracted in oxine solution

Line	As-solutionized		As-aged		$Mn_{12}Si_7Al_5$		$h^2 + k^2 + l^2$
	d (Å)	I/I_0	d (Å)	I/I_0	d (Å)	I/I_0	
1	4.455	15	4.463	30	4.50	50	8
2	3.976	45	3.987	60	4.02	70	10
3	3.639	10	3.648	15	3.665	30	12
4	3.352	35	3.376	20	3.395	30	14
5	3.182	5	—	—	—	—	—
6	2.969	5	2.978	10	2.996	10	18
7	2.816	10	2.822	10	2.838	30	20
8	2.686	5	2.684	5	2.712	10	22
9	2.468	20	2.476	30	2.490	50	26
10	2.339	60	2.336	10	2.356	10	28
11	2.293	10	2.307	25	2.315	50	30
12	2.224	10	2.225	5	2.246	10	32
13	2.156	70	2.164	80	2.176	90	34
14	2.099	40	2.104	40	2.115	60	36
15	2.039	100	2.046	100	2.057	100	38
16	1.986	10	1.994	5	2.006	40	40
17	1.940	10	1.948	5	1.958	10	42
18	1.856	15	1.863	5	1.869	90	46
19	1.777	5	1.787	5	—	—	—
20	1.747	5	1.748	5	1.759	20	52
21	1.652	5	1.656	5	1.665	30	58
22	1.544	15	1.555	5	1.56	20	66

TABLE IV X-ray data from aluminium alloy 2011, solution heat-treated 2 h at 520° C and aged 4 h at 315° C; extracted in oxine solution

Line	d (Å)	I/I_0	$CuAl_2$			Bi card		
			d (Å)	I/I_0	$h k l$	d (Å)	I/I_0	$h k l$
1	4.293	100	4.29	48	1 1 0			
2	3.284	80				3.28	100	1 0 2
3	3.197	30						
4	3.033	50	3.033		2 0 0			
5	2.818	2						
6	2.739	2						
7	2.456	66						
8	2.371	100	2.37	46	1 2 1			
9	2.273	30				2.273	41	1 1 0
10	2.145	30	2.145		2 2 0			
11	2.117	80	2.12	73	1 1 2			
12	2.089	10						
13	2.050	15						
14	1.962	5				1.970	10	1 1 3
15	1.919	70	1.91	100	1 3 0			
16	1.899	60			2 0 2			
17	1.868	5				1.868	23	0 2 2
18	1.813	2						
19	1.692	2						
20	1.655	2						
21	1.636	2				1.639	9	2 0 4
22	1.609	10	1.61	9	2 2 2			
23	1.506	10	1.51	7	1 3 2			
24	1.490	10				1.491	13	1 1 6
25	1.442	5				1.443	16	2 1 2

Table IV continued

TABLE IV continued

Line	$d(\text{Å})$	I/I_0	CuAl$_2$			Bi card		
			$d(\text{Å})$	I/I_0	$h\,k\,l$	$d(\text{Å})$	I/I_0	$h\,k\,l$
26	1.409	5	1.41	7	1 4 1			
27	1.393	5	1.393		1 2 3			
28	1.355	10	1.36	11	2 4 0			
29	1.328	5				1.330	11	1 2 4
30	1.288	30	1.29	15	4 0 2			
31	1.232	30	1.23	16	3 3 2			
32	1.220	5	1.22	6	0 0 4			
33	1.185	5				1.1843	2	0 2 8
34	1.092	6				1.0932	4	3 0 6
35	1.070	5	1.07	13	1 5 2			
36	1.059	2	1.06	5	2 2 4			
37	1.040	2	1.04	5	3 5 0			
38	1.030	5	1.03	14	1 3 4			
39	1.028	2	1.03	14	1 3 4			
40	1.010	1	1.01	7	6 0 0			
41	0.906	2				0.9065	2	1.1.12
42	0.893	2	0.892		2 6 2			
43	0.809	2	0.809		5 5 2			

complete, particularly for small d-spacings, that an accurate determination of the lattice parameters could be made. Using the method of Klein et al. [16], lattice parameters of $a = 6.064\,\text{Å}$ and $c = 4.874\,\text{Å}$ were obtained for the extracted CuAl$_2$ as compared with $a = 6.066\,\text{Å}$ and $c = 4.874\,\text{Å}$ for bulk CuAl$_2$ [17]. The effects of compositional and manufacturing variables on the lattice parameters of the precipitate phases can in this way be studied. The differences observed here for the CuAl$_2$ are not, however, appreciably large.

4. Conclusion

It has been shown that extraction of second phases in aluminium alloys is possible by galvanostatic dissolution of the matrix in an oxine solution. By this method, quantities of extracted precipitates sufficient for X-ray analysis are readily obtained. The usefulness of this method is, of course, limited to those compounds which are not soluble in the oxine solution.

Acknowledgements

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